

Studies in the Chelates of Some Less Common Transition Metals, II. Mitt.:

Os(VIII), Au(III)

By

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Low spin square planar complexes of Au(III) with five keto anils as ligands have been investigated spectroscopically. Several bands corresponding to $d-d$ and $L \rightarrow M$ charge transfer transitions have been identified following the "Molecular Orbital Scheme" given by Gray and Ballhausen. Square planar geometry established spectroscopically has been confirmed magnetically. Os(VIII) complexes involving d^0 configuration have also been studied and found having octahedral stereochemistry. Infrared spectra of ligands and complexes have been used to determine their structures and seats of coordination.

Introduction

Extensive studies have been carried out in the field of transition metal complexes of Schiff's bases, in their solutions and on solids as well. Upadhyay et al.¹⁻³ have also studied recently transition metal anil complexes. Present communication in continuation to the previous work deals with the magnetic and spectroscopic properties of hitherto rarely investigated⁴⁻⁶ Os(VIII) and Au(III) complexes. Based on these studies, low spin octahedral stereochemistry may be assigned to Os(VIII) complexes. Au(III) complexes are typical square planar involving low spin d^8 configuration of metal ion. Structures of the complexes have been established using infrared spectral data.

Experimental

All the anils precipitated either at room temperature or at low temperature, from the solutions in ether, containing both reactants (primary amine and aryl glyoxal) in equimolar quantities. Products were washed with cold ether and recrystallised from CHCl_3 . Complexes were isolated following the method of Upadhyay². Chemicals used in the preparations were B.D.H. or J.M. (London) products. Composition of anils and complexes were established by their analysis for nitrogen and metal (Table 1) performed at C.D.R.I., Lucknow (India).

Complex	Bands cm ⁻¹	Assignment	$10^6 \times \chi_g$ c.g.s. units	N, % Calc. Found	Metal, % Calc. Found								
1 OsO ₂ B ₂ Cl ₄	17,544 20,408 32,787 40,000	Charge Transfer	— 25.320	4.97 4.81	16.90 16.05								
2 OsO ₂ D ₂ Cl ₄	17,857 21,276 31,250 40,816					Charge Transfer	— 7.23	2.45 2.23	16.67 16.38				
3 AuACl ₃ · H ₂ O	20,833 22,222 25,974 31,746 40,000									¹ A _{1g} → ¹ A _{2g} → ¹ B _{1g} Spin forbidden Charge transfer ¹ A _{1g} → ¹ A _{2u} → ¹ E _{2u}	— 0.37	3.98 4.09	28.09 27.92
4 AuBCl ₃ · H ₂ O	17,857 18,867 21,053 26,316 28,169 40,000									¹ A _{1g} → ¹ A _{2g} → ¹ B _{1g} Spin forbidden Charge transfer ¹ A _{1g} → ¹ A _{2u} → ¹ E _u			
5 AuCCl ₃ · H ₂ O	20,408 21,276 22,727 23,809 25,641 30,303 40,000	¹ A _{1g} → ¹ A _{2g} → ¹ B _{1g} Spin forbidden Charge transfer ¹ A _{1g} → ¹ A _{2u} → ¹ E _u	— 12.08	2.15 1.99	29.65 28.00								
6 AuDCl ₃ · H ₂ O	21,739 24,390 25,641 31,250 40,000	¹ A _{1g} → ¹ A _{2g} → ¹ B _{1g} Spin forbidden Charge transfer ¹ A _{1g} → ¹ A _{2u} → ¹ E _u				— 4.06	1.98 1.86	27.78 26.98					
7 AuECl ₃ · H ₂ O	20,408 21,276 23,000 28,571 40,000	¹ A _{1g} → ¹ A _{2g} → ¹ B _{1g} → ¹ A _{2u} → ¹ E _u							— 16.27	1.85 1.70	26.06 26.32		

Magnetic measurements on the solid powders were made with *Gouy's* balance, at Delhi University, Delhi (India). Infrared spectra of the compounds under study were recorded on Perkin-Elmer Spectrophotometer X-621 model in Nujol mull using CsF optics at I.I.T., Kanpur (India), while U.V. and visible spectral observations were noted at A.M. University, Aligarh (India) with Beckman spectrophotometer DUX model using acetonitrile solutions.

Results and Discussion

Atomic susceptibility (χ_g) values of Os(VIII) complexes (Table 1) are suggestive of their diamagnetic nature, in agreement with the expected behaviour of low spin octahedral complexes of this ion with d^0 configuration. In the electronic spectra all the observed bands would correspond only to charge transfer, since in d^0 configuration permissible $d-d$ transitions are absent.

Au(III) ion with eight electrons generally almost invariably forms four coordinate low spin square planar complexes and hence are diamagnetic. Spin pairing is facilitated by the large extension of 5 d electron clouds into space. In the valency bond language such complexes involve dsp^2 hybridisation, and in crystal field nomenclature they almost always belong to strong field class. The χ_g values (Table 1) of Au(III) complexes under study show low spin square planar configuration of metal ion in them.

In the molecular orbital scheme⁵ of square planar complexes of d^8 configuration involving ligands having no π orbitals, viz. X^- , NH_3 , H_2O etc. (X^- = halogen ion), the $(n-1) d_{x^2-y^2}$, ns , np_x , np_y orbitals of metal ion will overlap ns , np_x , np_y (n = principal quantum number of ultimate shell of metal or donor atom) σ orbitals of ligands, giving rise to four bonding and four antibonding orbitals. Aforesaid metal orbitals occupied by eight coordinated electrons from ligands, the latter remaining empty, will correspond to four bonding orbitals, while metal's d_{xy} , $d_{xz}(d_{yz})$ and d_{z^2} orbitals are nonbonding receiving eight metal electrons all paired. Each ligand under study has two donor sites, one at azomethine ($C=N$) nitrogen and other at carbonyl ($C=O$) oxygen in which π orbitals are absent and both of them will make their σ orbitals available for overlapping with empty metal orbitals. Each of the two coordinating chlorine atoms also forms four bonding and four antibonding orbitals like nitrogen and oxygen atoms of ligand. *Gray and Ballhausen*⁵ in the electronic spectra of square planar complexes involving d^8 low spin ion and ligands having no π orbital system, discussed in general the existence of five bands, three corresponding to spin allowed $d-d$ transitions ($^1A_{1g} \rightarrow ^1A_{2g}$, $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1E_g$) and remaining two with high extinction coefficients and spaced at energy difference of $10,000\text{ cm}^{-1}$, arising due to $L \rightarrow M$ charge transfer spin allowed transitions ($^1A_{1g} \rightarrow ^1A_{2u}$ and $^1A_{1g} \rightarrow ^1E_u$). An attempt on the

Table 2. *Infrared Frequencies*

<i>A</i>	$\text{AuACl}_3 \cdot \text{H}_2\text{O}$	<i>B</i>	$\text{OsO}_2\text{B}_2\text{Cl}_4$	$\text{AuBCl}_3 \cdot \text{H}_2\text{O}$	<i>C</i>	$\text{AuCCl}_3 \cdot \text{H}_2\text{O}$
1740 m	1648 s	1720 m, sh	1688 m	1688 s	1714 s	1682 s
1708 m, sh	1620 s	1700 s	1638 m	1632 s	1696 s	1640 s
1618 m	—	1600 m	—	—	1604 m	—
—	1653 s, sh	—	1608 m, b	1600 s, b	—	1588 s
—	—	1563 w, sh	1553 m	1558 m	1558 m	—
1516 m	1518 s	1518 m, sh	1508 m, b	1513 s, sh	1523 w	—
816 m	820 m	800 s	817 m	800 m	814 m	816 s
—	490 w	—	428 w	478 m	—	468 m
—	340 m	—	320 m	338 s	—	338 s
—	318 w	—	294 m	308 s	—	304 m

A = p-Diethylaminoanil of 3-phenanthryl glyoxal; *B* = p-Diethylaminoanil of 9-anthracyl glyoxal; *C* = p-Chloroanil of 9-anthracyl glyoxal; *D* = p-Bromoanil of 9-anthracyl glyoxal; *E* = p-Iodoanil of 9-anthracyl glyoxal.

appearance of some spin forbidden $d-d$ and charge transfer transitions was also made by them. However, in Au(III) complexes only three bands could be identified and assigned viz., $^1A_{1g} \rightarrow ^1A_{2g}$, $^1A_{1g} \rightarrow ^1A_{2u}$ and $^1A_{1g} \rightarrow ^1E_u$. Making a thorough perusal of electronic spectral^{5,6} reports on Au(III) complexes, the spectra of all the five Au(III) complexes in question have been interpreted. Two bands appearing in U.V. region and having peak difference $\approx 10,000 \text{ cm}^{-1}$ in each complex have been assigned to spin allowed charge transfer transitions $^1A_{1g} \rightarrow ^1A_{2u}$ and $^1A_{1g} \rightarrow ^1E_u$ arising from $L \rightarrow M$ charge transfer. But only on the basis of limited knowledge⁵⁻⁷ about $d-d$ transitions taking place in Au(III) ion, the assignment of bands appearing in visible region has been made tentatively (Table 1). One band invariably at $\approx 25,600 \text{ cm}^{-1}$ almost in all cases is possibly due to spin forbidden charge transfer transition. In the visible spectrum closely spaced peaks with lower intensity as compared to their neighbour, may be considered a part of the latter and splitting may be accounted for considering the effect of high spin-orbit coupling.

The infrared spectra of complexes and their parent ligands exhibited bands, characteristic of the stretching vibrations of $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}=\text{C}$ (aromatic), 1 : 4 disubstitution, $M-\text{N}$, $M-\text{Cl}$ and $M-\text{O}$ (Table 2). $\text{C}=\text{O}$ and $\text{C}=\text{N}$ bands in complexes are shifted to lower frequencies. This gives an evidence that coordination occurs via carbonyl oxygen and azomethine nitrogen atoms. The bands corresponding to

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